REPRESENTATION OF THE EQUATION OF STATE OF A REAL GAS BY ELEMENTARY FUNCTIONS, AND METHODS OF THEIR DETERMINATION

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ELEMENTARY FUNCTIONS, AND METHODS OF THEIR DETERMINATION

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The equation of state of a real gas in terms of elementary

functions is derived over a wide range of density variation,

including the saturation curve and the liquid phase region,

from experimental data of the gas phase. The equation is

valid for the entire one-phase region, including the liquid

phase. The temperature functions, derived from the gas phase

data, are used to describe the liquid phase. Calculation by

computer is outlined, with reference to nitrogen.

The method of representing the equation of state in terms of elementary

functions was proposed in its original form as long ago as 1954 (Bibl.1). It

was later successfully used for an analytic description of the thermodynamic be-

havior of many real gases (Bibl.2 - 8). During this period, the method of de-

termining the elementary functions was modified and improved but has not yet at-

tained the necessary level of perfection. To make our exposition complete, we

will also present elementary considerations on the justification of the method.

The thermodynamic relation

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V,$$

written for the case of independent variables T and V, when twice integrated,

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** Numbers in the margin indicate pagination in the original foreign text.

leads to the following form of the equation of state:

$$P = A_0(V) + A_1(V)T + Q(T, V),$$ (1)

where the function $Q(T, V)$, obtained as a result of double integration, characterizes the curvature of the isochoric sections of the surface of state of a real gas and is small by comparison with the linear part of the equation, $A_0(V) + A_1(V)T$, which is confirmed by experiment.

According to the general Bogolyubov-Mayer theorem, the right-hand side of the equation of state is a power series in density $1/V$, whose coefficients (termed virial) depend on the temperature. It follows that the functions $A_0(V)$ and $A_1(V)$ are power series (practically polynomials) in density $1/V$ with constant coefficients, while the function $Q(T, V)$ is a series in $1/V$ with temperature-dependent coefficients.

For an analytic description of the function $Q(T, V)$ with the necessary accuracy, it is convenient to represent it in the form of a sum of products of functions with separated variables, i.e.,

$$Q(T, V) = \Sigma B_i(V) \Phi_i(T).$$ (2)

Studies show that it is often possible to confine the calculation to a single term on the right-hand side of eq.(2); however, if two terms are retained, then eq.(1) will describe the experimental data of a real gas with high accuracy over a wide range of temperature and pressure variation.

Passing to the dimensionless coordinates $\tau = T/T_c$, $\omega = V_c/V$, $\sigma = PV/RT_c$ /130 and confining ourselves to two terms for the description of the curvilinear part of $Q(T, V)$ of eq.(1), we obtain, after introducing new symbols,

$$\sigma = \alpha_0 + \alpha_1\tau + \beta\psi + \gamma\varphi.$$ (3)

where the functions α_0, α_1, β and γ depend only on ω, while ψ and φ, in accord-

ance with the general theory, are decreasing functions of the temperature not containing τ in the zeroth and first order.

Let us assume that the temperature functions ψ and φ are known as monotonically decreasing functions of the temperature, and that we also know the corresponding volume elementary functions α_0, α_1, β, γ at which eq.(3) satisfies the experimental data on the compressibility of a real gas over a wide range of variation of its parameters. We will call all these elementary functions "true". Starting from the structure of eq.(3), two lemmas readily amenable to direct verification can be formulated.

<u>Lemma 1</u>. The introduction into eq.(3) of new functions $\bar{\beta}$, $\bar{\gamma}$ which are linear combinations of "true" β and γ preserves the validity of the equation and may lead to new temperature functions which are linear combinations of the "true" ψ and φ.

<u>Lemma 2</u>. The replacement of the "true" temperature functions ψ and φ or of their linear combinations by new $\bar{\psi}$, $\bar{\varphi}$ in the form of

$$\bar{\psi} = a_0 + a\tau + \psi, \quad \bar{\varphi} = b_0 + b\tau + \varphi, \quad \Big| \tag{4}$$

where a_0, a, b_0, b are arbitrary constants, does not impair the validity of eq.(3) and only leads to the new functions $\bar{\alpha}_0$, $\bar{\alpha}_1$, which are connected with the "true" functions in the following way:

$$\bar{\alpha}_0 = \alpha_0 - a_0\beta - b_0\gamma, \quad \bar{\alpha}_1 = \alpha_1 - a\beta - b\gamma. \tag{5}$$

These lemmas continue to hold, regardless of the number of functions in the curvilinear part of eq.(3). This permits us to propose a simple and convenient method of analytic determination of the volume elementary functions α_0, α_1, β, γ, ... by the aid of the equations of isotherms which will be termed basic in what follows. The number of base isotherms should be equal to the

3

number of volume elementary functions; they are selected in the region in which the most reliable experimental data have about the same or a greater extent in density ω.

The base isotherms are analytically described in the form of polynomials in density ω; to satisfy the critical point and the critical conditions, one of the isotherms selected will be the critical isotherm whose equation satisfies these conditions.

For the case of two temperature functions in the curvilinear part of the equation, let us take four isotherms at the temperatures τ_1, τ_2, τ_3, τ_4, and write the system of four equations in the form

$$\alpha_0 + \alpha_1 \tau_i + \beta \psi(\tau_i) + \gamma \varphi(\tau_i) = \sigma_i, \tag{6}$$

where i takes the values 1, 2, 3, 4 in increasing order of temperature (the subscript 1 relates to the critical isotherm), while σ_i is the analytic expression of the ith isotherm in the form of a polynomial in ω.

Eliminating α_0, α_1 from the system of equations (6), we obtain on the left-hand side true combinations of "true" β and γ, and on the right-hand side their corresponding analytic expressions. We take one of these expressions as the /131 function $\bar{\beta}$, and the other as the function $\bar{\gamma}$; thus, we have solved the problem of determining the volume functions of the curvilinear part of eq.(3).

To determine the elementary functions of the linear part of eq.(3), let us make use of Lemma 2, from which it follows that the values of the new functions $\bar{\psi}$ and $\bar{\varphi}$ on two isotherms may be arbitrarily assigned. Two of the four basic isotherms, for example τ_1 and τ_4, are taken for this purpose.

Let us rewrite eq.(3), substituting the "true" functions by new ones

$$\sigma = \bar{\alpha}_0 + \bar{\alpha}_1 \tau + \bar{\beta}\bar{\psi} + \bar{\gamma}\bar{\varphi}. \tag{3'}$$

In accordance with the preceding, let us take, on the isotherms τ_1, τ_4,

4

$$\bar{\psi}(\tau_1) = \bar{\varphi}(\tau_1) = \bar{\psi}(\tau_4) = \bar{\varphi}(\tau_4) = 0.$$

after which, from eq.(3'), we obtain for these isotherms:

$$\bar{\alpha}_0 + \bar{\alpha}_1 = \sigma_1, \quad \bar{\alpha}_0 + \bar{\alpha}_1 \tau_4 = \sigma_4. \tag{7}$$

In the system of equations (7), let us substitute σ_1, σ_2 by their analytic expressions, and let us find $\bar{\alpha}_0$ and $\bar{\alpha}_1$; thereby all four volume functions have been determined in eq.(3'). The temperature functions $\bar{\psi}$ and $\bar{\varphi}$ along the non-basic isotherms remain unknowns. They may be determined from the available experimental data on each isotherm, for example by the method of least squares. It is simpler, however, to use the more convenient method of linearization, which is as follows:

Let us rewrite eq.(3') in the form of

$$\frac{\sigma - \bar{\alpha}_0 - \bar{\alpha}_1 \tau}{\bar{\beta}} = \bar{\psi} + \frac{\bar{\gamma}}{\bar{\beta}} \bar{\varphi}. \tag{8}$$

If, from the experimental data, we plot on each isotherm the left-hand side of eq.(8) against the quotient $\bar{\gamma}/\bar{\beta}$, we should obtain a straight line whose characteristics equal the values of $\bar{\psi}$ and $\bar{\varphi}$ on the given isotherm. If, however, we obtain distinctly curved lines on the isotherms, this indicates that it is insufficient to use only two terms in the curvilinear part of the equation of state; one more term and a fifth base isotherm must be introduced. On the other hand, it may also happen that $\bar{\beta}$ is proportional to $\bar{\gamma}$ and that the quotient $\bar{\gamma}/\bar{\beta}$ remains practically constant. This means that, in the curvilinear part of the equation, we must retain only a single term and use only three base isotherms.

In fact, in accordance with eq.(8), all cases considered up to now result in straight lines, which must be so drawn as to minimize the scattering of the test points and yield optimum agreement with the experimental data, making certain at the same time that the values of $\bar{\psi}$ and $\bar{\varphi}$ lie on smooth curves depend-

5

ing on the temperature.

Having obtained the graphs of the functions $\bar{\psi}$ and $\bar{\varphi}$ over the entire
temperature range for which data are available, let us set up the analytic expressions of these functions according to eq.(5) in the form of

$$\bar{\psi} = a_0 + a\tau + \frac{a_1}{\tau} + \frac{a_2}{\tau^3} + \dots + \frac{a_n}{\tau^n}, \quad \bar{\varphi} = b_0 + b\tau + \frac{b_1}{\tau} + \\ + \frac{b_2}{\tau^2} + \dots + \frac{b_m}{\tau^m}.$$

(9)

For good satisfaction of the values found for the functions $\bar{\psi}$ and $\bar{\varphi}$, let us take a sufficient number of terms in eqs.(9), with the stipulation that the functions on the base isotherms assume the prescribed values. In eqs.(9), the polynomial in $1/\tau$ can be replaced by other decreasing functions of the temperature, if they yield satisfactory agreement in a simpler manner.

Let us substitute the analytic expressions (9) into eq.(3') and collect the terms in τ in the zeroth and first order, which will reduce this equation to the form of eq.(3) in which the factors before $\bar{\beta}$ and $\bar{\gamma}$ are monotonically decreasing functions of temperature.

The equation of state, set up in this manner, will fully agree with the experimental thermal data, including the saturation curve, provided that the equations of the base isotherms are sufficiently accurate. It can also be asserted that the equation will be in satisfactory agreement with the caloric quantities, since analogous equations obtained by a less improved method have been in good agreement with these data, as has been verified repeatedly.

However, it is possible to ensure optimum agreement with the experimental caloric data if they are represented sufficiently, using them in deriving the equation of state for correcting the temperature functions by their first and second derivatives. The calculated expressions for the enthalpy resulting from

6

eq.(3') contain the first derivatives of the functions $\bar{\psi}$ and $\bar{\varphi}$, while the calculated expressions for the heat capacity c_p contain the second derivatives as well, so that these derivatives can be determined from the experimental caloric data (as the functions $\bar{\psi}$ and $\bar{\varphi}$ themselves are determined from the thermal data), which we have described in detail elsewhere (Bibl.2).

At the present time, equations of state must not only properly describe the thermal and caloric experimental data, but must also give reliable results at high temperatures (3000°K and above) for which there are no experimental data in existence.

To extrapolate an equation of state to the high-temperature region, a reliable method of extrapolating the functions $\bar{\psi}$ and $\bar{\varphi}$ to this region must be found. The extrapolation may be performed by the aid of the second virial coefficient, which can be calculated by methods of statistical physics. The problem is facilitated by the fact that the curvilinear part of eq.(3'), at high temperatures, is described with sufficient accuracy by a single term, i.e., the functions $\bar{\psi}$ and $\bar{\varphi}$ become equal. Since the linear part of the second virial coefficient is known from the equation of state (3'), the curvilinear part and /133 thus also the temperature function, is easily determined from its values found by the statistical method.

Using the above-described method, the equation of state can be set up over a wide range of density variation, embracing the saturation curve and the region of the liquid phase, provided that the data in this range, at supercritical temperatures, are represented in the form of a rectangular net of isotherms and isochores. There are many cases, however, in which the experimental data in the gas phase for $\tau > 1$ are given in the form of a rectangular net of isotherms and isobars at restricted densities, and no experimental data exist for densi-

ties corresponding to the liquid phase. The liquid phase itself, at subcritical temperatures, is represented by data in a narrow interval of density variation on each isotherm, which shifts into the region of increasing values of ω with decreasing temperature.

To obtain, in this case, the equation of state represented in terms of elementary functions over the entire range of density variation, we must proceed as follows:

From the experimental data of the gas phase, using the method described above, we construct an equation of state that is valid up to a certain density ω_0, determined by these experimental data. In this equation, the temperature functions are determined in the entire temperature interval for which data exist, including low temperatures of the order of the normal boiling point and below it.

General considerations connected with the continuity of the gaseous and liquid state, as well as experimental verification, show that the entire one-phase region, including the liquid phase, can be described by the aid of an equation represented in terms of elementary functions.

It may be concluded from this that the temperature functions, derived from data of the gas phase, may be used to describe the liquid phase. This makes it possible to determine, by the method of least squares, the volume functions over all density variations, i.e., the coefficients of the polynomials in terms of which they are represented. However, in connection with the large number of unknown coefficients so obtained, the only way the problem can be solved is with a computer.

To simplify the problem, it is suggested to separately describe the liquid phase by means of the equation

$$\sigma_f = \alpha_{of} + \alpha_{1f}\tau + \beta_f\bar{\psi} + \gamma_f\bar{\varphi}, \tag{10}$$

where the temperature functions $\bar{\psi}$ and $\bar{\varphi}$ coincide with the corresponding functions of the gas phase. The unknowns in eq.(10) are the volume elementary functions α_{of}, α_{1f}, β_f, and γ_f, or more accurately the coefficients of the polynomials in density ω, describing these functions. Prescribing the number of terms in each of these polynomials, the coefficients may be determined by the method of least squares from the experimental data of the liquid phase and the lower boundary curve, provided the functions $\bar{\psi}$ and $\bar{\varphi}$ in eq.(10) are known.

To obtain a smooth course of the functions on transition from the gas to the liquid phase, it must be stipulated that, at a density ω_0, not only the values of the corresponding functions of the gas phase and liquid phase shall coincide but also their first derivatives. To obtain also a smooth course of the isotherms and elementary functions at high densities, the equations for both phases must not only satisfy the experimental data themselves but also the /134 Maxwell rule, with acceptable accuracy, for the isotherms $\tau < 1$. With this object, the condition equations designed to satisfy the experimental data of the liquid phase should include a certain number of condition equations expressing the Maxwell rule.

The above-described method of constructing the equation of state has given satisfactory results in practical use. In particular, the method has been used by A.A.Vasserman to describe the thermodynamic properties of nitrogen from the experimental data (Bibl.9 - 11).

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